

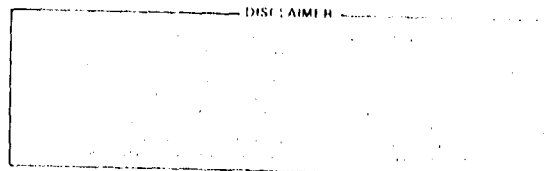
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**TITLE:** SUPERCOMPUTER REQUIREMENTS FOR THEORETICAL CHEMISTRY

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**MASTER**

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SUPERCOMPUTER REQUIREMENTS

FOR

THEORETICAL CHEMISTRY

by

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ABSTRACT

There are many problems important to the theoretical chemist which, if implemented in their full complexity, would strain the capabilities of today's most powerful computers. Several such problems are now being implemented on the CRAY-1 computer at Los Alamos. Examples of these problems will be taken from the fields of molecular electronic structure calculations, quantum reactive scattering calculations, and quantum optics.

## I. INTRODUCTION

The electronic computer is undeniably an essential component in the tool bag of the modern theoretical chemist and, with ever improved accessibility to more powerful computing, it is tempting to feel a sense of euphoria about current computer capabilities. At Los Alamos, we have a truly impressive resource of large computers -- at present we have a choice of two 1-million word CRAY machines and four CDC 7600 machines. However, even with this powerful a computing environment, the main objective of this talk is to ask whether or not this current euphoria is really justified. Have we yet reached the stage where we can, with current computers, address problems which are traditionally thought of as chemistry? The answer is, in many cases, no.

In this talk, we survey three areas of theoretical chemistry which receive considerable attention at the Theoretical Chemistry and Molecular Physics Group at Los Alamos. These three areas are (1) molecular electronic structure calculations, (2) chemical dynamics calculations, and (3) quantum optics and spectroscopy. In introducing each category, we will note the types of mathematical algorithms used to solve problems typical of each area. We then present examples of types of calculations which we feel are at the current state-of-the-art. Finally, we will present a wish list of problems in each category which we would like to be able to study, but are simply beyond current computing capabilities.

The program of this symposium makes it clear that there will be several talks to follow which will concentrate specifically on problems associated with electronic structure calculations -- we will only skim over the subject for now. We will concentrate more heavily on problems in chemical dynamics, and conclude with problems in quantum optics.

## II. MOLECULAR ELECTRONIC STRUCTURE CALCULATIONS

In determining the quantum mechanical structure of a molecule, there are three major steps (roughly equal in difficulty) to be attacked computationally (See Fig. 1.). We first define a set of atomic basis functions centered at each nucleus and then compute a large number of integrals over these basis functions. This information feeds into the construction of the Fock matrix. The eigenvalues of the Fock matrix are associated with the total energy of the system. The eigenvectors define the occupied orbitals of the system and the eigenvalues define the orbital energies. This information is used to construct a new Fock matrix, which is again diagonalized. This procedure is repeated iteratively until the total energy of the system is minimized and the orbitals are constant from one iteration to the next.

Reasonable determinations of molecular structure can be obtained at this SCF-level of calculation. However, for an accurate determination of the structure and properties of molecules, correlations between the motions of the many electrons of the system must be included. To do this, many-electron wavefunctions are computed using sums of products of these one-electron orbitals. This process is the configuration interaction (CI) method; getting accurate CI wavefunctions and energies requires an enormously large basis of SCF functions. The Hamiltonian matrix in this basis is constructed and diagonalized to get the accurate CI wavefunctions and energies. The CI matrix tends to be both very large and very sparse. Efficient computer codes must take into account the sparsity of the CI matrix both in its construction and diagonalization phase.

Let's turn our attention to the computational needs of the structure problem (See Fig. 2). Defining  $n$  as the number of atomic basis functions employed, there are several characteristic matrices to consider. The Fock matrix, which we repeatedly construct and diagonalize until convergence, is only an  $n \times n$  matrix; unfortunately, to construct this matrix at each iteration of the SCF procedure, we have to process the  $n^4/8$  two-electron integrals. At the current state of the art, the number of atomic basis functions  $n$  tends to be about 100. This limitation is not so much because of the difficulty of diagonalizing  $100 \times 100$  matrices, but because of the IO limitations inherent with processing the tens of millions of integrals at each iteration.

It is easy to see why the CI step is time consuming. Although the Fock matrix is only  $n \times n$ , the size of the CI matrix goes more like  $n^4$ ! Now the CI matrix is very sparse, as indeed it has to be, if we are to get some of the eigenvectors and eigenvalues of matrices which can get to be as large as  $10000 \times 10000$ . Most of the electronic structure work at LASL is concentrated on the CDC 7600 machines. We are currently adapting our programs to use the CRAY machines efficiently, but it appears the CRAY's will not be more than 10 times as powerful as a 7600. It isn't hard to think of problems which would overwhelm the CRAY's.

In Fig. 3, we consider a few problems of interest to the structure chemist in the area of transition metal chemistry. The molecules we consider here are of interest for their bonding properties and their electronically excited states. The  $\text{Re}_2\text{Cl}_8^-$  ion has a strong (almost quadruple)  $\text{Re} \equiv \text{Re}$  bond -- we estimate that we can do a fair job of determining the energy of this ion with about 1/2 hour of CRAY time, using about 100 orbitals in a split-valence basis. Not all the electrons

in this system would be treated explicitly. At LASL, we regularly treat large Z atoms using effective core potentials to eliminate the innermost core electrons from the calculation.<sup>1</sup> Using about 250 orbitals, we can treat this mixed-valence ruthenium-pyrazine complex. This complex is of interest because of its metal-organic bonding and the fact that the two ruthenium atoms are not equivalent to each other, even at the Hartree-Fock level. Of interest also is this bridged rhodium complex, which we estimate we can tackle with about 350 orbitals. This molecule has the interesting property that, when dissolved in water, it liberates hydrogen gas in the presence of sunlight. This would be a very tough problem, even for the CRAY -- we estimate 60 hours of CRAY time to determine the structure.

One of the more relevant duties of the structure chemist is to provide potential energy surfaces to the chemical dynamicist. The potential energy surface is determined by computing the electronic energies of the molecular system as a function of the nuclear geometry. In addition, if several electronic states participate in the collision dynamics, it may also be desirable to have available certain matrix elements between electronic surfaces. Now dynamicists tend to be rather demanding -- at least by request of not also by need. Consequently, we arrive at this first law of potential surface calculations -- the structure chemist gets bored with running his program long before he can satiate the dynamicist. (Paraphrased from Fig. 4.) But look what happens -- even if the dynamicist compromises to the point that he settles for 10 points per nuclear degree of freedom, it nevertheless requires a bundle of structure calculations to generate a surface for a relatively simple A+BC type reaction. Now suppose we had a dynamicist

who dared to study a four-body reaction, like  $AB+CD$ . Then imagine a structure chemist willing to compute a million points on a potential surface. It shouldn't be surprising that there is at present only one potential surface which has been computed at enough points and enough accuracy to satisfy the dynamicist -- the simplest of all neutral molecular systems -- the  $H+H_2$  surface computed by Bowen Liu and Per Siegbahn.<sup>2</sup> Because of the high symmetry of this system, they have calculated a surface at about 250 points (instead of the 1000 estimated).

### III. QUANTUM CHEMICAL DYNAMICS

Let's now turn our attention to the requirements of the chemical dynamicist. Here we consider only quantum mechanical approaches to chemical reaction dynamics, and only mention that there also exists a considerable computational technology which treats chemical dynamics by using classical mechanics.

The only type of chemical reaction we are likely to ever be able to solve rigorously in a quantum mechanical way is a three-body reaction of the type  $A+BC \rightarrow AB+C$ . (See Fig. 5.) The input information to the dynamicist is the potential energy surface computed by the quantum structure chemist. Given this potential surface, we treat the nuclear collision dynamics using Schrödinger's equation to model the chemical reaction process.

As was mentioned earlier, there is only one fully ab initio potential energy surface for chemical reaction available to the dynamicist. This surface is appropriate for an  $A+BC$  reaction where A, B, and C are all three hydrogen atoms or hydrogen isotopes (H, D, T). Fig. 6 shows a contour map of the collinear part of this surface (all three nuclei lie on a single line); the essential features of the surface topology are

the entrance valley, the product valley, and the activation barrier separating these two valleys. Motion perpendicular to each valley corresponds to vibration of the reactant or product molecule, and motion parallel to the floor of the valley measures progress of the reaction, from reactants to products. The classical mechanical solution to chemical reaction dynamics is accomplished in fact by solving for the motion of a point mass particle on this hypersurface. Reaction corresponds to a trajectory which starts out in the reactant valley, crosses the barrier, and ends moving out into the product valley.

Quantum mechanically, the reactive dynamics is expressed in a more wavelike language. By solving Schrödinger's equation, we treat the problem where an initial probability wave of reactants is sent in towards the activation barrier from reactants. When the wave hits the barrier, part of it is reflected and part of it is transmitted. The reflected part of the wave corresponds to non-reactive collision events, and the transmitted part corresponds to reaction.

The actual equations we solve are called the close-coupled equations. (See Fig. 7.) They are obtained from the Schrödinger equation in the following way: (1) we first define all but one of the coordinates of the system to be "target" coordinates and the final coordinate is called the "scattering coordinate" or "reaction coordinate." The reaction coordinate tells us where we are in our journey along the potential surface from the reactant valley towards the product valley. Basis functions are defined which describe motion in all the target coordinates. These basis functions are square integrable for the target coordinate degrees of freedom, but the function which describes motion in the reaction coordinate is determined numerically. The equations



for these scattering functions are the close-coupled equations. These equations are a set of coupled second order linear ordinary differential equations. The difficulty in solving problems in quantum chemical dynamics is simply this -- how many coupled equations are there? The answer is that there is one equation for every "channel" in the close coupling expansion.

Each channel is defined by a unique set of quantum numbers for the target degrees of freedom. There are five such labels for each channel. They are (1)  $J$  -- the total angular momentum and (2)  $M$ , its projection on an axis fixed in space. In addition there are labels (3)  $n$  for the vibrational motion of the molecule, (4)  $j$  for the molecular rotational degree of freedom, and (5)  $l$  for the atom-molecule orbital angular momentum. The equations for one set of  $(J,M)$  are uncoupled from equations for other values of  $(J,M)$ . The equations for a function labeled by one value of  $(n,j,l)$  are coupled to values of all the other functions labeled by (the same or) different values of  $(n,j,l)$ . The number of coupled equations we have to solve therefore depends on the number of molecular vibration-rotation states we have to treat in the scattering dynamics at each collision energy.

In the next paragraph, we present a rudimentary look at the algorithm we use to solve these coupled equations. This method is called R-matrix propagation;<sup>3</sup> and although there are several other methods equally capable of solving the coupled equations, we use R-matrix propagation as an example because it illustrates the kind of computer algorithms we require. The R-matrix itself contains the scattering information we need; the final R-matrix is assembled in a recursive fashion using the analytic solution of the scattering problem over a

small region of the scattering coordinate. The algorithm works in the following way: given (1) an old R-matrix associated with the solution of the scattering problem over one region of space; and given (2) a sector R-matrix which defines the scattering solution over a small incremental region of space, we can (3) assemble a new R-matrix which is associated with the solution of the scattering problem over the (old + incremental = new) region of space. The recursion equation is a matrix equation of order n,

$$R_2 = r_{22} + r_{21}(R_1 + r_{11})^{-1}r_{12}$$

where there are n channels in the close-coupling expansion of the wavefunction. As you can see, this recursion formula involves very standard matrix operations -- multiplication and inversion. The analytic solution of the coupled equations in the incremental region is defined in terms of the eigenvalues and eigenvectors of the coupling matrix. So you can see that the basic numerical algorithm we require our supercomputer to handle effectively are standard matrix operations -- multiplication, diagonalization, and inversion. All these algorithms go asymptotically as  $n^3$  -- and so the complexity of the quantum dynamics' problem is measured (as we said previously) by the size (n) of the close coupled equations.

So let's return our attention again to the question of the size of the coupled equations and consider some examples. Many of the chemical reactions we are interested in are dominated by an activation barrier which separates the reactant and product valleys of the potential energy hypersurface. (See Fig. 8.) The energy of this activation barrier

locates the general energy range of interest to the reaction  $\mu$ -micist -- because there isn't very much reaction at energies below the barrier height, where only quantum tunnelling processes can contribute to reaction. But, as we show schematically in Fig. 8, there may be several molecular energy states below the activation barrier. All these states, at the very least, must be included in the close coupling expansion.

Let's now consider several examples. The simplest of all reactions is the  $H+H_2$  reaction. The  $H_2$  vibrational levels are fairly widely spaced, but we must also include the rotational manifold of levels associated with each vibrational level. (See Fig. 9.) Now, it is this rotational manifold of levels (and the degeneracies of states associated with each vibration-rotation level) which ultimately breaks the bank in the size of the close coupling expansion.

In order to treat quantum dynamical problems, it will be necessary to introduce approximations which reduce the size of the set of coupled equations. Two promising approximations are the centrifugal sudden (CS)<sup>4,5</sup> approximation and the infinite order sudden (IOS) approximation.<sup>5,6</sup> The CS approximation removes the coupling between the  $j$  and  $\ell$  angular momenta, thereby reducing the size of the coupled equations from  $n$  to approximately  $n^{1/2}$ . In this approximation, each  $(n,j)$  energy level generates only one channel instead of  $(2j+1)$  channels. The more drastic IOS approximation appears to be promising for systems in which the molecular species rotates very slowly on the scale of the collision time. This approximation removes in effect all the rotational levels from the system.

For the  $\text{H}+\text{H}_2$  system, we estimate that we can just about solve this easiest of all problems with current state-of-the-art computers at the 100-channel level. If we can use the CS approximation for this system, we can in fact go to quite high scattering energies.

But remember that  $\text{H}+\text{H}_2$  is the simplest of all reactions. Moving more in the direction of true chemistry, consider next a reaction for which only two nuclei are hydrogens (instead of three) -- the  $\text{F}+\text{H}_2$  reaction. This reaction is over 1 eV exothermic in going from the reactant valley, over a small (1 kcal) barrier, to the product valley. The exothermicity of reaction means that there are several energetically accessible (open) vibrational channels for this system even at the threshold for reaction. If we include all the rotational levels with each vibration, and the proper  $(2j+1)$  rotational degeneracies, we have an unthinkably large number of coupled equations to solve -- over 1200 channels. (See Fig. 10.) To solve this problem, we must use approximations such as the CS approximation, which reduces the problem to the much more manageable 100-channel level.

For our final quantum dynamics example, consider what happens when we substitute a lithium atom for one of the remaining hydrogens -- the  $\text{Li}+\text{FH}$  reaction. (See Fig. 11.) This semiempirical potential surface (collinear) shows a narrow entrance channel vibrational valley, a shallow well in the entrance channel, a barrier, and a broad product vibrational valley. Even using the CS approximation, the energy level diagram for this reaction makes this problem accessible only to the full power of a CRAY level machine. Anyone foolish enough to tackle the problem rigorously will have to face a 10000-channel system at energies just above threshold!

The moral of our story of the quantum chemical reaction dynamicist should be perfectly clear -- at least two hydrogens are the dynamicists best friend. Indeed, our current supercomputers may seem to be a bit less super.

#### IV. QUANTUM OPTICS

The interaction of molecules with electromagnetic radiation is of fundamental interest to the chemist. When the electromagnetic field is relatively weak, we can describe these interactions using perturbation theory. The study of single photon transitions induced between molecular states by weak fields is the province of the molecular spectroscopist. But now, with the ever more powerful radiation fields available from laser technology, we are in a position to study the interaction between molecules and electromagnetic radiation at intensities too large for perturbation methods to work. The somewhat broader field of quantum optics seeks to describe the time evolution of molecules in the presence of these intense fields. Of course, before we can follow the migration of energy among the various degrees of freedom of a (possibly large) molecule, we must first know what the electronic, vibrational, and rotation energy states of the molecule are in the absence of any radiation field. The effect of the field is to move population from the initial molecular state into other molecular states in a time dependent way. The solution of this problem can be obtained by solving the time-dependent Schrödinger equation, so long as the molecule we are studying is modeled at zero pressure. At finite pressures (when collisions are present) the Schrödinger picture is too difficult to solve directly; in this case, we can model the incoherent (phase destroying) effects of collisions upon the coherent excitation induced by the electromagnetic

field by resorting to a Bloch equation (or density matrix) formalism. Collisions are modelled by decay rates not only in the diagonal (but also the off-diagonal) terms of the density matrix. We also have one further constraint in developing methods to treat problems in quantum optics -- because laser pulses last for a relatively long time in comparison to the time associated with molecular vibration and rotation, we must solve our time-dependent Schrödinger or Bloch equation in a way which gives answers efficiently for long times.

Consider for a moment the Bloch equation for the density matrix,  $\underline{\rho}$ ,

$$\dot{\underline{\rho}} = \underline{\rho}\underline{H} - \underline{H}\underline{\rho} - \underline{\Gamma}\underline{\rho}$$

The Bloch equation gives the time derivative of the density matrix  $\underline{\rho}$  in terms of its commutator with the Hamiltonian for the system, and the decay rate matrix  $\underline{\Gamma}$ . Each of the matrices,  $\underline{\rho}$ ,  $\underline{H}$ , and  $\underline{\Gamma}$  are  $n \times n$  matrices if we consider a molecule with  $n$  vibration-rotation states. We solve this equation by rewriting the  $n \times n$  square matrix  $\underline{\rho}$  as an  $n^2$ -element column vector. Rewriting  $\underline{\rho}$  in this way transforms the  $\underline{H}$  and  $\underline{\Gamma}$  matrices into an  $n^2 \times n^2$  complex general matrix  $\underline{R}$ . We obtain

$$\dot{\underline{\rho}} = \underline{R}\underline{\rho}$$

The solution of the transformed equation is obtained by exponentiating this  $\underline{R}$  matrix. To efficiently exponentiate this matrix we must first diagonalize it, exponentiate the eigenvalues, and back transform with the eigenvectors. This back transformation procedure is repeated for every time at which we wish to know the molecular populations.

A typical problem of interest at Los Alamos is the solution of the infrared multiple photon excitation dynamics of sulfur hexafluoride. This very problem has been quite popular in the literature in the past few years.<sup>7</sup> The solution of this problem is modeled by a molecular Hamiltonian which explicitly treats the asymmetric stretch  $\nu_3$  ladder of the molecule coupled implicitly to the other molecular degrees of freedom. (See Fig. 12.) We consider the the first seven vibrational states of the  $\nu_3$  mode of  $\text{SF}_6$  ( $6\nu_3$ ); the octahedral symmetry of the  $\text{SF}_6$  molecule makes these vibrational levels degenerate, and coupling between vibrational and rotational motion splits these degeneracies slightly. Furthermore, there is a rotational manifold of states associated with each vibrational level. Even to describe the zeroth-order level states of this molecule is itself a fairly complicated problem. Now if we were to include collisions in our model of multiple photon excitation of  $\text{SF}_6$ , we would have to solve a matrix Bloch equation with a minimum of  $84^2 \times 84^2$  elements. Clearly such a this problem is beyond our current abilities, so in fact we neglect collisional effects in order to stay with a Schrödinger picture of the excitation dynamics.

In the Schrödinger picture, we can include the diagonal elements of the  $\tilde{L}$  matrix, which model the coupling of the explicitly treated  $\nu_3$ -ladder states with the other implicitly treated molecular states. The exponentiation of the coupling matrix in the Schrödinger picture requires the diagonalization of an  $n \times n$  complex general matrix. Populations at several times are computed by the back transformation method, and a quadrature over time of those populations gives the leakage of amplitude into the  $\text{SF}_6$  quasicontinuum degrees of freedom. This whole process is repeated for each new initial rotational state  $J_0$ , laser

frequency  $\nu$ , and laser intensity  $I$ . Our calculations at LASL can require up to 10 hours of 7600 time for each laser power of interest.

There are several other interesting topics in quantum optics which we would like to be able to study. For example, we would like model problems in double resonance spectroscopy, where there are two electromagnetic fields with possibly different polarizations simultaneously interacting with a molecule. This problem resembles the multiple photon excitation problem in that there is population migration along ladders of states, but in this case there can be a vastly larger number of quantum levels to treat -- on the order of  $2(2J+1)$ . At room temperature, the most probable value of  $J$  for  $\text{SF}_6$  is about 60, which implies a 250 state calculation.

Finally, we also mention a substantially more complex problem -- that of laser pulse propagation through an absorbing medium. In this case we are asking not only what happens to the molecule in the presence of an electromagnetic field, but also what happens macroscopically to the field in the presence of the molecule. The solution of this problem requires treating the multiple photon dynamics problem self-consistently with a solution of Maxwell's equation over a grid of points in space.

## V. CONCLUSIONS

In summary, our intention has been to give examples of the types of problems we are interested in at LASL. Our appetite for computationally difficult problems has not been dulled by the current availability of computer resources. In the area of molecular electronic structure calculations, we need computers for which there can be written efficient algorithms to diagonalize large matrices, and in the case of CI calculations, we need efficient indirect addressing capabilities (gather-



scatter operations) in order to process these matrices whose elements are 99% zeroes. Either we need efficient IO capabilities in order to process the lists of millions of integrals, or it has to be cheaper to calculate these integrals as we go along.

In the area of quantum dynamics, we need again computers capable of efficiently performing standard types of matrix operations (inversion, diagonalization, multiplication) on large matrices of the order of several hundreds.

And in the area of quantum optics, we need similar types of capabilities - standard matrix manipulations - but now our matrices are complex general instead of real symmetric.

In each of the fields discussed here, state-of-the-art calculations require the full capabilities of modern computers. Newer supercomputers will need to be several orders of magnitude more powerful to efficiently attack many of the problems currently facing the theoretical chemist.

## References

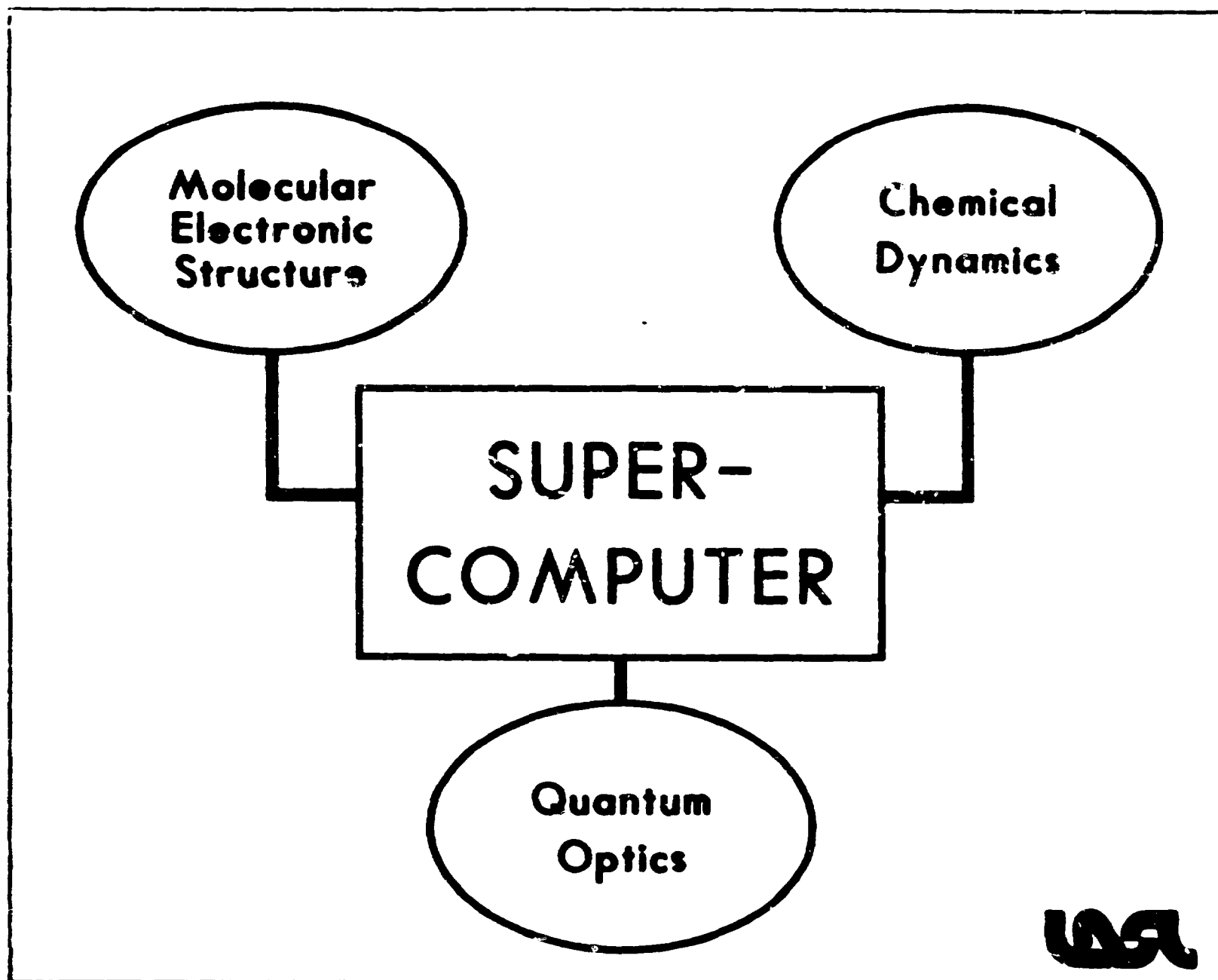
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### Figure Captions

- Fig. 1. Schematic representation of three areas of theoretical chemistry. We will consider the relationship between each of these areas and the modern supercomputer.
- Fig. 2. Computational requirements for molecular electronic structure calculations.
- Fig. 3. Examples of problems in transition-metal chemistry.
- Fig. 4. Potential energy surface calculations for the chemical dynamicist.
- Fig. 5. Quantum chemical dynamics. Scope and method of currently tractable problems.
- Fig. 6. Contour map of the  $\text{H}+\text{H}_2$  collinear chemical potential energy surface.
- Fig. 7. How close coupled equations are obtained in chemical dynamics problems.
- Fig. 8. Schematic representation of chemical potential energy surface. Counting of states below reaction barrier for both reactants and products gives a minimal estimate of numbers of coupled equations to be solved.
- Fig. 9. Counting of channels for the  $\text{H}_3$  reaction. Reaction barrier is at 0.4 eV; state-of-the-art calculations are performed to slightly above 1 eV. Arrows are drawn whenever another 100 coupled channels are required.
- Fig. 10. Counting channels for the  $\text{FH}_2$  reaction. As in Fig. 9, except arrows count states for CS approximation (each vibration-rotation level counts only once). Reaction threshold is at 1.65 eV.

Fig. 11. Counting channels for the LiFH reaction. As in Figs. 9-10, arrows count states for CS approximation. Reaction threshold near 0.6 eV.

Fig. 12. Schematic of multiple photon excitation dynamics of  $\text{SF}_6$ . Groups of levels show lowest three  $\nu_3$  vibrational states. Higher states are split by rotational interactions with vibrational motion.



**USA**

# Computational Requirements

- Let  $n$  = # atomic basis functions

<u>Matrix</u>	<u>Size</u>	<u>Limits</u>	
		<u>7600</u>	<u>CRAY-1</u>
Fock	$n \times n$	100	300
$2 e^- \int$	$n^4/8$	$10^7$	$10^9$
CI	$\sim n^4 \times n^4$	$10^4$	$10^6$



## Problems in Transition-Metal Chemistry

<u>Molecule</u>	<u><math>n^*</math></u>	<u>Estimated CRAY time (hrs)</u>
$\text{Re}_2\text{Cl}_8^{2-}$	104	0.5
$[(\text{NH}_3)_5\text{Ru}]_2\text{-pyrazine}]^{5+}$	252	20
$[\text{Rh}-(\text{NC}-\text{C}_6\text{H}_4-\text{CN})_4-\text{Rh}]^{2+}$	340	60

\*split-valence basis using effective potentials



## Potential Surfaces for Comical Dynamics

**Law of Nature:** Dynamicists will always want more points on a potential energy surface than one is willing to calculate.

**Response of Electronic Structure Practitioners:**  
Dynamicists will usually settle for 10 points / degree of freedom.

	Points
Triatomics	$10^3$
Tetratomics	$10^6$





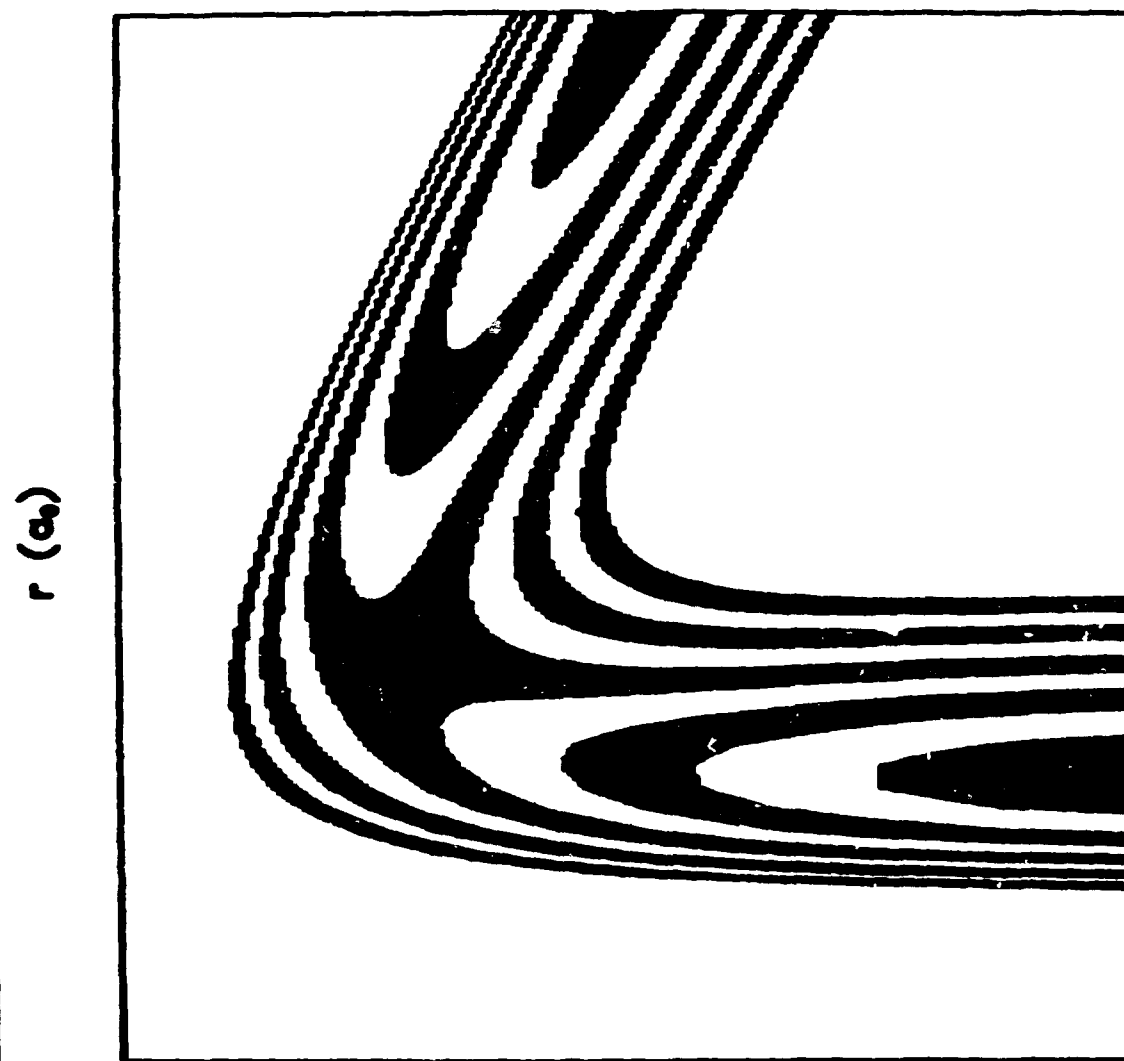
# Quantum Chemical Dynamics

- $A + B-C \rightarrow A\cdots B\cdots C \rightarrow A-B + C$
- Requires potential energy surface(s) from electronic structure calculations
- Solve Schrodinger equation for dynamics

$$H\Psi = E\Psi$$



CONTOURS FOR THE SLTH - HHH POTENTIAL SURFACE



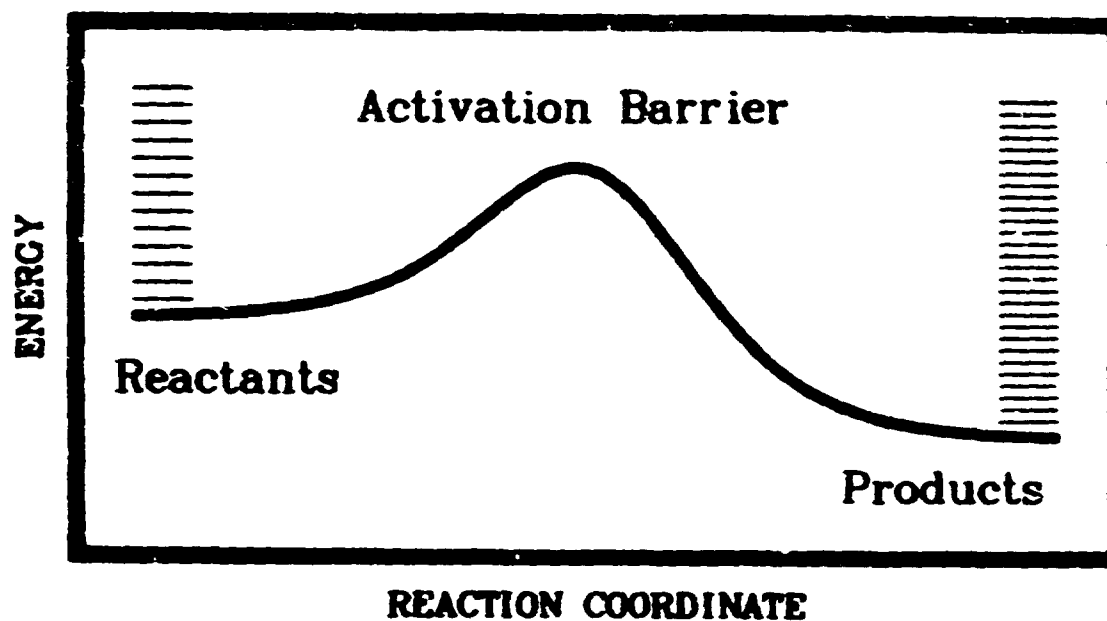
# Close-Coupled Equations

- Separate all  $(3N-3)$  coordinates into one scattering coordinate and  $(3N-3)-1$  internal coordinates
- Expand wavefunction using square integrable basis functions for  $(3N-3)-1$  coordinates and solve numerically for function of scattering coordinate.
- Leads to a set of coupled linear second order differential equations. One equation for each "channel."



## How Many Coupled Channels are There?

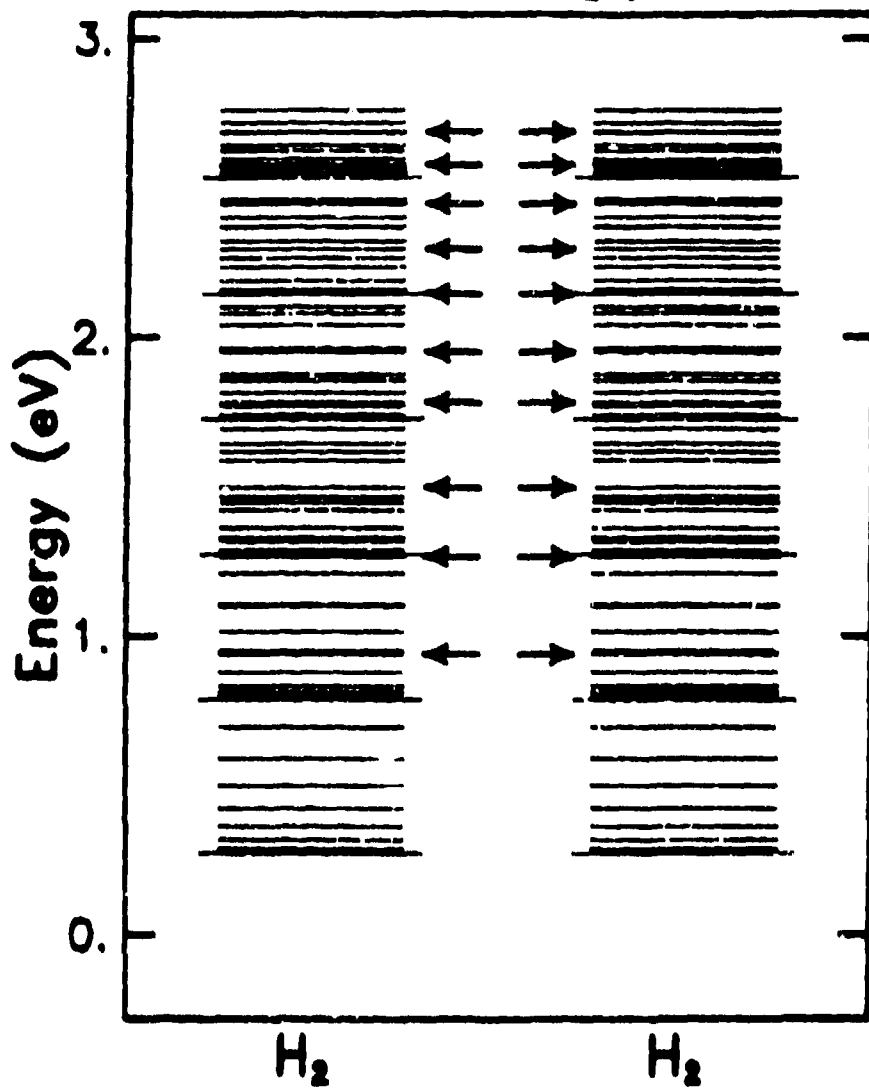
- Reactions are dominated by activation barriers

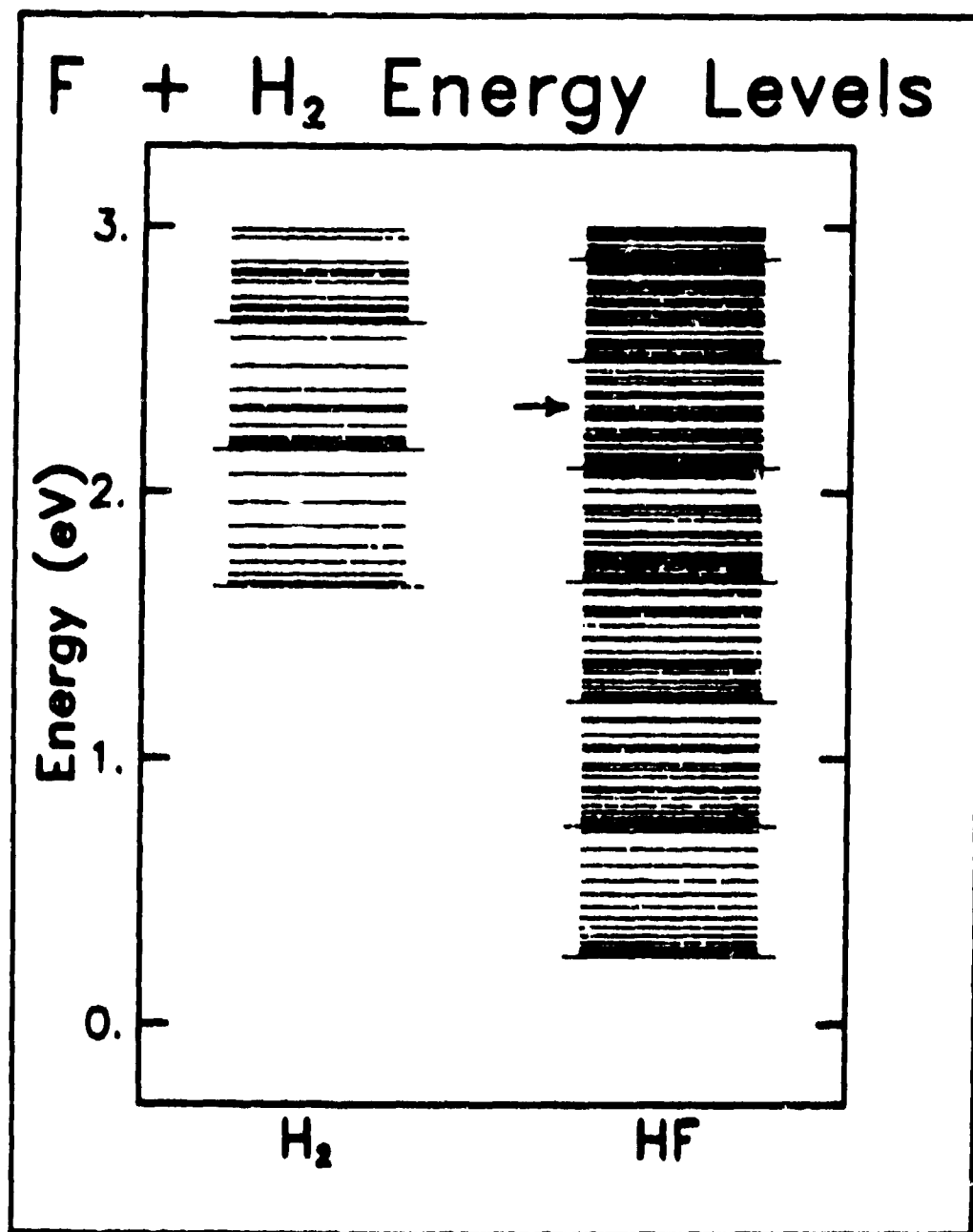


- Need all open channels, some closed channels
- State of art = 100 channels (CRAY = 300)

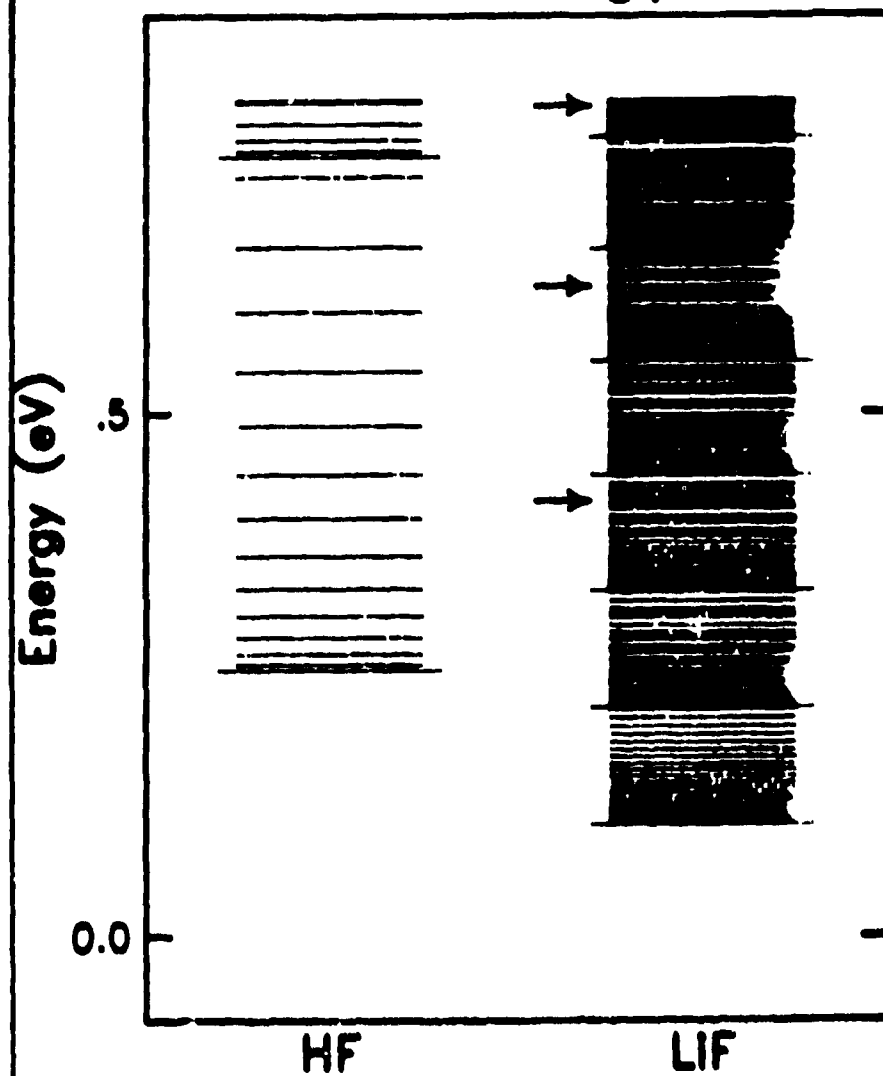
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# H + H<sub>2</sub> Energy Levels





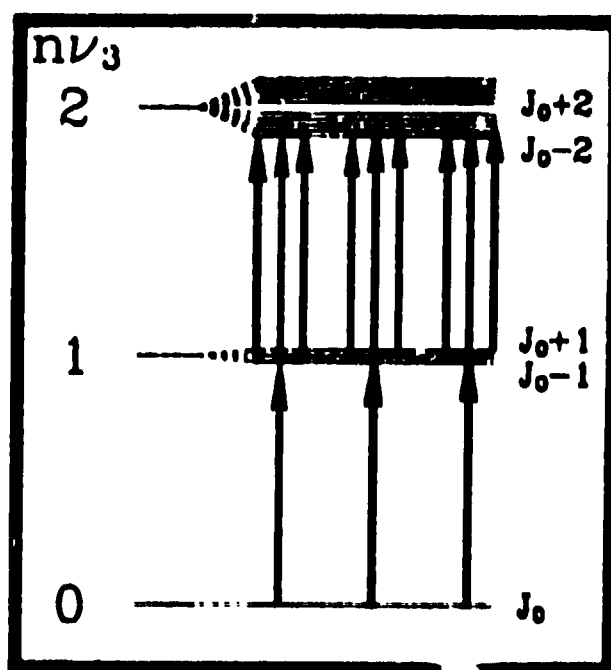
# Li + FH Energy Levels



## Multiple Photon Excitation ( $\text{SF}_6$ )



- Asymmetric stretch ( $\nu_3$ ) ladder dynamics



- Vibrational degeneracy is  $5(N+1)(N+2)$

- Include up to  $6\nu_3$  in H, get  
 $84^2 \times 84^2$  matrix to diagonalize

